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Studying Kinetics of the Dehydration Reaction of Pyruvic Acid and Ethyl Pyruvate Using the Polarographic Kinetic Currents

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New analyses of the kinetics of the dehydration reaction of pyruvic acid and ethyl pyruvate gem-diol group have been performed using the direct current polarographic data. The diffusion contributions of the depolarizer (as keto-form) from the bulk solution to the total limiting kinetic and diffusion currents have been taken into account. As a result, corresponding equations for the kinetic current and for the thickness of the reaction layer have been obtained. It was shown that the condition of the stationarity of the diffusion and chemical reactions is carried out that is necessary for using the equation of the kinetic current. The values of the rate constants of the dehydration of the *gem*-diol group calculated by us were close to the ones found by other methods.
Detailed analyses of the hydration equilibrium constants of the pyruvic acid keto-group allowed us to choose the most correct constants for kinetic calculations.

INTRODUCTION

Studying the kinetics of the hydration-dehydration reactions of pyruvic acid (PA) and its esters is of great interest for different biochemical processes and development of the methods for the investigation of the kinetics of fast chemical reactions.[1–13] Many methods, such as pressure[1–3] or temperature[4]-jump, nuclear[5–7] or proton[8] magnetic resonance, spectrophotometry,[9–11] pulse polarography[12] and direct current polarography[13] (DCP) have

been used to study the kinetics of indicated reactions with the participation of PA and its esters. At the same time, application of the DCP technique for PA[13] and its esters demands further additional developments. This is due to the fact that the contribution of the diffusion of the depolarizer (keto-form) from the solution bulk to the total limiting kinetic and diffusion currents have not been taken into account. At the same time, this effect has been recently taken into account by us for glyoxylic acid.[14] In addition, it should be noted that Koutecky's equation[15,16] has been used in the non-correct form[13] for the determination of the rate constant of the PA dehydration reaction.

Here, we present the further developed theory of the kinetic currents for the electroreduction of PA and ethyl pyruvate (EP) at the dropping mercury electrode using DCP, which enabled us to extract the correct rate constants of the PA and EA *gem*-diol group dehydration.

THEORETICAL PART

Electrode reactions of PA have been considered by us in strongly acidic solutions (pH=0) where it is fully undissociated. The dissociation constant of PA[17–20] at 25 °C pK_a = 2.47–2.49 (for the ionic strength I=0) and pK_a = 2.37 (I = 0.5). Thus, at pH = 0, undissociated molecules of PA and EA (undissociated form of EA exists also at different pH) participate in the electrode chemical reaction, which results in appearance of the kinetic current. This reaction is the gem diol/keto dehydrated transition.[12,13,21–24]

$$\textit{Gem}\text{-diol} \xrightarrow{k_d;-H_2O} \text{Keto} \xrightarrow{+2e^-;+2H^+} \qquad (1)$$

where k_d is the rate constant of the PA or EA *Gem*-diol – molecule dehydration.

The equilibrium constant of the hydration reactions of PA or EP molecules is expressed by Eq. (2):

$$K_h = [\textit{Gem}\text{-diol}] / [\text{Keto}] = k_h / k_d \qquad (2)$$

where k_h is the rate constant of the Keto-molecules hydration of PA or EP.

Since the K_h value does not strongly differ from the one (see below), Koutecky's equation in the more general form[15,16] should be used for the determination of k_d:

$$\bar{i}_l^{\,k} / (\bar{i}_l^{\,d} - \bar{i}_l^{\,k}) = 0.886\ [k_d(1 + K_h)t_1/K_h^{\,2}]^{0.5}\ . \qquad (3)$$

Where $\bar{i}_1^{\,k}$ and $\bar{i}_1^{\,d}$ are the average kinetic and diffusion limiting currents, respectively, t_1 is the drop time of the dropping mercury electrode.

Eq. (3) is correct when $\bar{i}_1^{\,k}$ is determined only by the rate of the chemical reaction (1) and by the diffusion of the electroinactive *Gem*-diol – molecules, and $\bar{i}_1^{\,d}$ is determined by the diffusion of *Gem*-diol – molecules. However, these conditions are not carried out for PA and EP, since the diffusion contribution of the depolarizer (Keto – molecules) from the bulk of the solution to the electrode surface is considerable. Therefore, the total kinetic ($\Sigma\,\bar{i}_1^{\,k}$) and diffusion ($\Sigma\,\bar{i}_1^{\,d}$) currents are larger than the values of $\bar{i}_1^{\,k}$ and $\bar{i}_1^{\,d}$, respectively:

$$\Sigma\,\bar{i}_1^{\,k} = \bar{i}_1^{\,k} + \bar{\chi}\,[\text{Keto}] \tag{4}$$

$$\Sigma\,\bar{i}_1^{\,d} = \bar{i}_1^{\,d} + \bar{\chi}\,[\text{Keto}]\,. \tag{5}$$

Where $\bar{\chi}$ is Ilkovic's constant.

Taking into account Eqs. (6)-(7)

$$\Sigma\,\bar{i}_1^{\,d} = \bar{\chi}\,([\textit{Gem}\text{-diol}] + [\text{Keto}]) \tag{6}$$

$$\bar{i}_1^{\,d} - \bar{i}_1^{\,k} = \Sigma\,\bar{i}_1^{\,d} - \Sigma\,\bar{i}_1^{\,k} \tag{7}$$

we can derive Eq. (8) using Eqs. (2) – (7):

$$[\Sigma\,\bar{i}_1^{\,k}\,(1 + K_h) - \Sigma\,\bar{i}_1^{\,d}]\,/\,(\Sigma\,\bar{i}_1^{\,d} - \Sigma\,\bar{i}_1^{\,k})\,(1 + K_h) =$$

$$0.886\,[k_d(1 + K_h)t_1 / K_h^{\,2}]^{0.5}\,. \tag{8}$$

Eq. (8) is the kinetic equation when the diffusion contribution of the depolarizer from the solution bulk to the electrode surface could not be neglected.

Eq. (8) allows to obtain the correct value of k_d using the experimental values of $\Sigma\,\bar{i}_1^{\,k}$, $\Sigma\,\bar{i}_1^{\,d}$, K_h and t_1. The $\bar{i}_1^{\,d}$ value can be also calculated from Ilkovic's equation using the diffusion coefficient as shown for glyoxylic acid.[14,25]

At K_h >>1 Eq. (8) takes the form:

$$(\Sigma\,\bar{i}_1^{\,k}\,K_h - \Sigma\,\bar{i}_1^{\,d})\,/\,(\Sigma\,\bar{i}_1^{\,d} - \Sigma\,\bar{i}_1^{\,k})\,K_h = 0.886\,(k_d t_1 / K_h)^{0.5}\,. \tag{9}$$

This means that the condition $K_h >> 1$ is not enough to use Koutecky's equation[15,16] in its usual form (Eq. (3) at $K_h >> 1$) as it was established by us for glyoxilic acid.[14] At the same time, we can obtain the usual Koutecky's equation from Eq. (9) using an additional condition: $\Sigma\,\bar{i}_1^{\,k}\,K_h >> \Sigma\,\bar{i}_1^{\,d}$:

$$\Sigma \bar{i}_l^{\,k} / (\Sigma \bar{i}_l^{\,d} - \Sigma \bar{i}_l^{\,k}) = 0.886 (k_d t_1 / K_h)^{0.5} . \quad (10)$$

Analogously to Koutecky's equation[15,16] (3) or (10), Eq. (8) or (9) are also based on the condition of the stationarity of the diffusion and chemical reactions. For fulfilment of this condition, it is necessary to reach the correlation:[26]

$$\mu_D / \mu_R \geq 3 \quad (11)$$

where μ_D and μ_R are the thickness of diffusion and reaction layers, respectively. The μ_D value is determined by equation[27] (12):

$$\mu_D = (3/7\pi D t_1)^{0.5} \quad (12)$$

where D is the diffusion coefficient. If the μ_R' value corresponds to the thickness of the reaction layer for the kinetic current without the contribution of the depolarizer diffusion from the solution bulk (Eq. (3)), Koutecky's equation[15] can be used for its calculation:

$$\mu_R' = [D (1+K_h) / k_d K_h^2]^{0.5} . \quad (13)$$

However, Eq. (13) cannot be applied for PA and EP systems since the diffusion contribution of the depolarizer from the solution volume is considerable.

To find the value of μ_R corresponding to Eq. (8) we used the method of Hanus,[28] which for electrode reaction (1) allows Eq. (14) to be written:

$$\Sigma \bar{i}_l^{\,k} = 10^{-3} n F \bar{q} D [\text{Keto}]_{so} / \mu_R \quad (14)$$

where $\bar{q}$ is the average mercury drop surface, $[\text{Keto}]_{so}$ is the concentration of Keto – molecules on the outside surface of the reaction layer where the equilibrium between *Gem*-diol and Keto molecules is still kept (Eq. (2)).

Using equations[27]

$$[Gem\text{-diol}]_{so} = (\bar{i}_l^{\,d} - \bar{i}_l^{\,k}) / \bar{\chi} \quad (15)$$

$$10^{-3} n F \bar{q} / \bar{\chi} = 0.886 (t_1 / D)^{0.5} \quad (16)$$

and Eqs. (2), (7), (14)–(16), we can obtain the expression for the calculation of μ_R when the diffusion contribution of the depolarizer is considerable:

$$\mu_R = 0.886 (D t_1)^{0.5} / y K_h \quad (17)$$

where

$$y = \Sigma \bar{i}_l^{\,k} / (\Sigma \bar{i}_l^{\,d} - \Sigma \bar{i}_l^{\,k}) . \quad (18)$$

The comparison of the μ_R' and μ_R values for PA and EP systems calculated from Eq. (13) and Eqs. (17, 18), respectively, reveals that $\mu_R' > \mu_R$. This can be explained by the additional diffusion contribution of the depolarizer in the case of μ_R. The same situation was observed for other systems.[29]

From Eqs. (12) and (17), we can derive equation 19:

$$\mu_D / \mu_R = 1.309 y K_h . \quad (19)$$

This equation allows to establish the availability of the stationarity of the diffusion and chemical reaction (based on the correlation (11)) and thus to distinguish the possibility of using Eq. (8). Note that at $\Sigma \bar{i}_l^{\,d} >> \Sigma \bar{i}_l^{\,k}$ the stationarity of diffusion and chemical reactions is carried out without fulfilment of correlation (11), as it was observed for glyoxylic acid.[14] However, for the PA and EP systems no correlation $\Sigma \bar{i}_l^{\,d} >> \Sigma \bar{i}_l^{\,k}$ takes place and therefore the verification of correlation (11) is necessary.

RESULTS AND DISCUSSION

Equilibrium Constants of the Hydration Reactions of Pyruvic Acid and its Esters

As it follows from Eq. (8), determination of the rate constant of dehydration reaction, k_d, requires to know the equilibrium constant of the hydration reaction, K_h, (Eq. (2)) for PA (undissociated form) and EP. The hydration concerns the keto-group. The equilibrium constants for PA, EP as well as for methyl pyruvate (MP) are shown in Table I. Many of these constants have been recalculated by us to 25 °C using Ref. 19 and data from Refs. 8 and 33.

In considering the hydration equilibrium constants, we should pay attention to the possible influences by the keto-enol toutomeric equlibria,[11,40,42] dimerization equilibria[43] and polymerization.[32,44] Unfortunately, these reactions have been studied only for PA. Since K_h values for PA, MP and EP are close (Table I), we can accept that all influences indicated above are not distinguished in the determination of K_h for PA, MP and EP. For PA, the equilibrium constants of enolization are very small, such as $(8–11) \cdot 10^{-6}$ for the anion[11,42] and $6.2 \cdot 10^{-4}$ for the molecule.[40] Thus, in determination of the K_h values, the effect of the enolization of the PA keto-form could be neglected. Muller and Baumberger[44] observed the appearance of a separate polaro-

TABLE I

Equilibrium constants of the hydration reaction of the carbonylic group of pyruvic acid molecules (PA), methyl pyruvate (MP) and ethyl pyruvate (EP) at 25 °C

C_{PA}, M	$2 \cdot 10^{-2}$	$4.8 \rightarrow 0$	2	1.25	~1	4.2	$10 \rightarrow 0$	$10 \rightarrow 0$	$11 \rightarrow 0$	$1 \cdot 10^{-3}$
K_h	*2.4*	3.1[a]	1.6[a]	1.2[b]	1.8[b,c]	0.65[a]	*2.5*	3,2	*2.4*[a]	*2.1*
Method[d]	S	NMR	NMR	NMR	NMR	NMR	PMR	PMR	NMR	PP
Ref.	21	30	31	32	18	5, 6	8	8, 19	33	12
C_{PA}, M	$8 \rightarrow 0$	0.1	0.5	$1 \cdot 10^{-3}$	≤ 1	$8 \cdot 10^{-2}$	4.2	$2 \cdot 10^{-4}$	$9.9 \cdot 10^{-4}$	$1.1 \cdot 10^{-2}$
K_h	*2.2*[a]	1.9	*2.3*[a]	*2.4*[a]	2.0[b]	*2.3*	0.61[a]	> 1.4	*2.9*	*2.3*
Method[d]	NMR	PMR	NMR	DCP	RS	S	NMR	DCP	LSV	S
Ref.	7	34	35	36	37	38	39	13	13	40
C_{MP}, M	1	0.094								
K_h	3.1	2.9								
Method[d]	NMR	S								
Ref.	41	10								
C_{EP}, M	0.208	0.075								
K_h	2.4	2.4								
Method[d]	S	S								
Ref.	4	10								

a. The constants have been recalculated by us from the data of Ref. 19; b. Temperature is not indicated; c. 10% D_2O; d. S – Spectrophotometry, NMR – Nuclear magnetic resonance, PMR – Proton magnetic resonance, PP – Pulse polarography, DCP – Direct current polarography, RS – Raman spectroscopy, LSV – Linear sweep voltammetry.

graphic wave as a result of the PA polymerization at fairly low concentrations. However, this has not been confirmed by other polarographic studies,[22,23,36,45,46] probably because of the higher purity of PA and significantly lower solutions exposure in these Refs. Quantitative polarographic evaluation of the PA polymerization[44] has not been carried out correctly since the hydration of the carbonyl group has not been taken into account. Therefore, unlike Ref. 44, one can believe that the PA polymerization[31] as well as the PA dimerization[43] are appreciable only at high concentrations of PA. For example, for PA the equilibrium constant of dimerization is 0.55 (25 °C).[43] Hence, at $C_{PA} \leq 0.1$ M, we can not take into account the dimerization of PA. However, application of the nuclear-(NMR) or proton magnetic resonance (PMR) methods requires the use of high concentrations of PA. Therefore, the K_h values should be extrapolated to $C_{PA} = 0$ (Table I). The absence of this extrapolation led to a large scatter of the K_h values derived from NMR and PMR methods (Table I). It should be noted that the changes in the K_h values at high C_{PA} are also caused by variations in the concentration of H_2O, especially due to additional hydration of the PA molecules.[6–8,30,33]

As we believe, the most correct K_h values for PA lie in the interval between 2.1–2.9 (values from 10 different studies obtained by six different methods). These values are marked in Table I. The average value of K_h = 2.4 ± 0.1 (25 °C) for PA was used by us in kinetic calculations. The values of K_h = 2.1 and 2.9 have been derived from pulse polarographic[12] and linear-sweep voltammetry[13] methods, respectively. In contrast, the K_h values for the glyoxilic acid anion from pulse polarographic[12] and linear-sweep voltammetric[47] methods are close. At the same time, the K_h values that have been found in Ref. 36 and Ref. 13 using the DCP method are significantly different (Table I). More correct is the K_h value from Ref. 36. Probably, the kinetic contribution in the limiting current[36] at pH 2–3 is neglected. For EA, the K_h value is the same for the two determinations (Table I). Since some kinetic calculations have been also carried out at 22 °C, the values of K_h for PA and EP found at 25 °C have been recalculated to 22 °C. Thus, we found that for PA K_h = 2.7 at 22 °C using the data from Ref. 19 and K_h = 2.6 (22 °C) for EA based on the data from Ref. 10.

Kinetics of the Dehydration Reactions of Pyruvic Acid and Ethyl Pyruvate

The rate constants of the *gem*-diol group dehydration of PA (undissociated molecules) and EP have been calculated on the basis of polarographic (DCP) limiting kinetic currents ($\Sigma \bar{i}_l^k$) at pH = 0 for PA[22,23,36,45,46] and EP[36] and at pH = 2–5 for EP[36] (Table II). Moreover, the value of $\Sigma \bar{i}_l^k$ from Ref. 46 (Table II) was found from $\Sigma \bar{i}_l^k / (\Sigma \bar{i}_l^k)_{pH=4}$ using the $(\Sigma \bar{i}_l^k)_{pH=4} / (\Sigma \bar{i}_l^d)$ value.[22,23] This is sufficiently correct since values $(\Sigma \bar{i}_l^k)_{pH=4}$ and $\Sigma \bar{i}_l^d$ are close.

The $\Sigma \bar{i}_l^d$ values (Table II) have been found by us from Ilkovic's equaiton[27] using the data for the mercury capillary (Table II) and the diffusion coefficient of PA, $D = 9.7 \cdot 10^{-6}$ cm$^2 \cdot$ s^{-1} from Ref. 12 (pulse polarography). The same diffusion coefficient was accepted for EP. As it could be expected, the diffusion coefficient of glyoxylic acid from Ref. 25, $D = 1.01 \cdot 10^{-5}$ cm$^2 \cdot$ s^{-1}, is close to the diffusion coefficient of PA. The experimental $\Sigma \bar{i}_l^d$ value at pH > 10 from Ref. 36 was not used by us since it was not confirmed by the data from Ref. 46.

Calculations of the dehydration rate constants (k_d) (Table II) were carried out on the basis of the kinetic equation (8) obtained by us when the diffusion contribution of the depolarizer from the solution bulk was taken into account (see Theoretical part).

The values of k_d (Table II) found by us are three times (for pH = 0) and ten times (for pH 2–5) smaller than the k_d values calculated from Koutecky's equation[15,16] (3) when $\bar{i}_l^k$ and $\bar{i}_l^d$ were replaced by $\Sigma \bar{i}_l^k$ and $\Sigma \bar{i}_l^d$, respectively.

Since the values of k_d obtained from Eq. (8) are close to the data found by other methods (except for the data from Ref. 45), we can conclude that Eq. (8), unlike Koutecky's equation[15,16] (3), allows to derive the correct value of the rate constants of the PA and EP dehydration on the basis of the DCP method. Lower value of k_d from Ref. 45 (Table II) is a result of significantly higher PA concentration (20mM), which leads to either the changes in D value or to the inapplicability of Ilkovic's equation.

The values of k_d at pH = 0 (Table II) could be considered as the rate constant of the PA or EP dehydration when the catalysis of the hydronium ions (k_d^H) is the predominant rate constant, since $k_d^H >> k_d^{H_2O}$ ($k_d^{H_2O}$ is the rate

TABLE II

Rate constants of the dehydration reaction of the gem-diol group of the pyruvic acid molecules (PA) and ethyl pyruvate (EP) obtained using direct current polarographic data and the ratio between the thickness of the diffusion and reaction layers

PA or EP	t °C	C_{PA} or C_{EP} mM	m mg $\cdot$ s^{-1}	t_1 s	pH	$\Sigma \bar{i}_l^k$ μA	Ref.	$\Sigma \bar{i}_l^d$ μA	K_h	k_d s^{-1}	μ_D / μ_R
PA	25	20	1.39	3.16	0	65.9	45	113.7	2.4	0.31	4.3
PA	25	0.44	1.52	2.12	0	1.8	22, 23	2.48	2.4	2.5	8.3
PA	25	0.5	2.4	3.75	0	3.2	46	4.20	2.4	2.2	10.0
PA	22	1.0	2.92	2.70	0	6.4	36	9.07	2.7	2.0	8.5
EP	22	1.0	2.92	2.70	0	7.1	36	9.07	2.6	4.8	12.3
EP	22	1.0	2.92	2.70	2–5	3.6	36	9.07	2.6	$3.5 \cdot 10^{-2}$	2.2

constant in the catalysis of H_2O, see Table III) and $[H^+] \approx 1$ M at pH = 0 (Ref. 49). Thus, at pH = 0, we can write:

$$k_d = k_d^H \tag{20}$$

and find (using data from Table II) that for PA k_d^H = (2.0–2.5) $M^{-1} \cdot s^{-1}$ at 22–25 °C and for EP k_d^H = 4.8 $M^{-1} \cdot s^{-1}$ at 25 °C. These constants are close to those obtained from other methods, *i.e.*, k_d^H = (2.0–2.7) $M^{-1} \cdot s^{-1}$ at 23.5–25 °C for PA and k_d^H = (2.8–5.9) $M^{-1} \cdot s^{-1}$ at 25 °C for EP (Table III). The high value of k_d^H = 8.7 for PA from Refs. 5 and 6 (Table III) can not be compared with constants indicated above because of high concentration of PA (4.2 M) which was used in the NMR method.[5,6]

As it was shown by Floury *et al.*[36] for EA the value of $\Sigma \bar{i}_1^k$ does not depend on pH at pH 2–5 (Table II). Hence, for this pH interval and low C_{EA} = 1 mM (Ref. 36) the k_d constant is close to $k_d^{H_2O}$:

$$k_d = k_d^{H_2O} . \tag{21}$$

Thus, from Table II for EA we can find that $k_d^{H_2O} = 2.5 \cdot 10^{-2}$ s^{-1} (DCP method), which is close to $k^\circ_d = 3.7 \cdot 10^{-2}$ s^{-1} found by the spectrophotometric

TABLE III

Catalytic rate constants of the dehydration reaction of gem-diol group of the pyruvic acid molecules (PA) and ethyl pyruvate (EP) obtained by different methods

PA or EP	t / °C	C_{PA} or C_{EP} / M	k°_d / s^{-1}	k_d^H / $M^{-1} \cdot s^{-1}$	Method[a]	Ref.
PA	25	~0.1	0.22	2.5[b]	PJ	1, 2
PA	25	–	0.14[c]	2.7[c]	PJ	3
PA	24	4.2	–	8.7	NMR	5, 6
PA	23.5	2.0	–	2.0	PMR	8
PA	25	$1.5 \cdot 10^{-2}$	$5.9 \cdot 10^{-2}$ [d]	–	S	9
PA	25	$1.0 \cdot 10^{-3}$	–	2.3[d]	PP	12
PA	25	$2.0 \cdot 10^{-4}$	5.1	–	DCP	13
EP	25	≤ 0.2	$\leq 1.3 \cdot 10^{-2}$	5.9	TJ	4
EP	25	–	0.11[c]	2.8[c]	TJ	48
EP	25	$7.5 \cdot 10^{-2}$	$3.7 \cdot 10^{-2}$ [e]	–	S	10

a. PJ – Pressure-jump, TJ – Temperature-jump, the other as in Table I; b. The k_d^H = 1.25 $M^{-1} \cdot s^{-1}$ from Refs. 1 and 2 has been corrected to k_d^H = 2.5 $M^{-1} \cdot s^{-1}$ in Ref. 8 ; c. The values have been recalculated by us from K_h using K_h = 2.4 (for PA and EP) (Table I); d. The values have been recalculated by us to 25 °C from k_h° using the activation energy from Refs. 1 and 8 and K_h = 2.4 (Table I); e. The values have been recalculated by us from k_h° using K_h = 2.4 (Table I).

method.[10] Since k°_{d} corresponds to the relatively low $C_{EA} = 7.5 \cdot 10^{-2}$ M (Table III), we can accept that under these conditions $k^{\circ}_{d} = k_{d}^{H_2O}$. This explains the above indicated closeness of the $k_{d}^{H_2O}$ (Table II) and k°_{d} (Table III) values. At the same time, other k°_{d} values (Table III) differ by the large scatter (especially constants found in Ref. 13).

In conclusion, we note that the stationarity of the diffusion and chemical reactions (1) at pH = 0 is realized since the condition (11) takes place (Table II). The μ_D / μ_R values have been calculated from Eq. (19). This confirms the possibility of using Eq. (8). However, at pH 2–5 (for EA), this conclusion can be used with some approximation (Table II).

CONCLUSIONS

1. Significant contribution of the diffusion of the depolarizen (keto-forms) from the solution bulk to polarographic kinetic currents has been found for the undissociated molecules of pyruvic acid and ethyl pyruvate. This does not allow the use of Koutecky's equation for kinetic calculations.

2. The new kinetic equation has been derived taking into account the diffusion contribution of the depolarizen.

3. The rate constants of the dehydration of the *gem*-diol group found from the correct kinetic equation are close to the data obtained by other methods.

4. It was shown that the condition of the stationarity of the diffusion and chemical reaction is realized, which is necessary for the use of the kinetic equation. This conclusion has been drawn from the equation of the thickness of the kinetic layer, derived by us taking into account the diffusion contribution of the depolarizen from the solution bulk.

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SAŽETAK

Istraživanje kinetike dehidratacije piruvične kiseline i etilpiruvata korištenjem polarografskih kinetičkih struja

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Provedene su nove analize kinetike dehidratacije piruvične kiseline i etil–piruvata na osnovi dc polarografskih podataka. Uzeta je u obzir difuzija depolarizatora iz mase otopine prema površini elektrode i njezin doprinos graničnim strujama difuzijskog i kinetičkog polarografskog vala. Pretpostavljeno je da u masi otopine depolarizator ima strukturu ketona. Postavljene su jednadžbe za kinetičku graničnu struju i za debljinu reakcijskog sloja uz površinu elektrode. Pokazano je da se u reakcijskom sloju uspostavlja ravnoteža između difuzijskog toka depolarizatora i brzine kemijske reakcije. Izračunane vrijednosti konstanti brzina dehidratacije *gem*-diolske grupe slažu se s podacima iz literature. Potanke analize konstanti ravnoteže dehidratacije ketonske grupe piruvične kiseline omogućile su točan izbor konstanti korištenih za računanje kinetičkih parametara te reakcije.